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Noncovalent attachment of oxide nanoparticles onto carbon nanotubes using water-in-oil microemulsions

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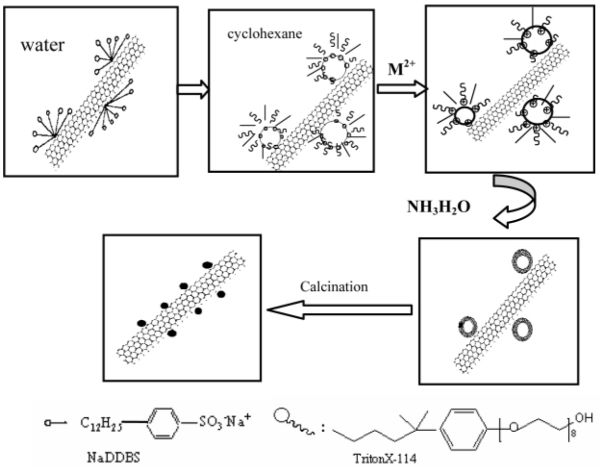
We report a simple and general noncovalent method for attaching ZnO and MgO nanoparticles onto MWNTs using water-in-oil microemulsions, which is important for preserving the mechanical and electrical properties of carbon nanotubes.

The unique mechanical, optical and electronic properties of carbon nanotubes offer many opportunities for their applications such as structure reinforcement,[1] nanoelectronic devices,[2] and field emitters.[3] The dispersion and sidewall functionalization of CNTs is becoming essential for these and other applications. Although CNTs have been included in a wide range of organic materials,[4] research on inorganic coating onto CNTs is rather limited. Recently, surface coverage with a layer or particles of SiO_2, SnO_2, Al_2O_3 and TiO_2 on CNTs has been reported.[5] However, so far, there is no flexible method that could functionalize CNTs with a broad varied composition. Herein, we propose an alternative, noncovalent method for surface coverage of MWNTs with ZnO and MgO nanoparticles using water-in-oil microemulsions. These modified MWNTs might find applications in field-emission display devices.[6]

Water-in-oil (W/O) microemulsions (*i.e.* reverse micelle solutions) are transparent, isotropic, thermodynamically stable liquid media. In these systems, fine microdrops of the aqueous phase are trapped within assemblies of surfactant molecules dispersed in a continuous oil phase. The domain size of the dispersed phase is usually very small (a few nanometres) and chemical reaction may occur within the nanodroplets or at the oil/water interface. In the past few years, many studies have been conducted on reverse microemulsion-mediated synthesis of polymeric nanoparticles,[7] and ultrafine ceramic particles.[8] The aim of this study is to demonstrate the feasibility of the microemulsion route for the surface coverage of CNTs with inorganic oxide nanoparticles.

The general strategy for covering CNTs with metal oxide particles is illustrated in Scheme 1. In detail, MWNTs (Chengdu Organic Institute, China) produced by catalytic decomposition were first dispersed by 0.5% NaDDBS (sodium dodecylbenzenesulfonate) in aqueous solution at a concentration of 14.5 mg ml^{-1}. The surfactant, Triton X-114 (Aldrich Chemical Company Inc.) was dissolved in cyclohexane at a ratio of 30 : 70 in a cylindrical flask, which was immersed in a water bath maintained at 40 °C and stirred for 30 min. Then, an aqueous solution of MWNTs was dropped into the oil phase with continuous stirring. After addition of the first drop, the next drop of aqueous solution was not added until the system returned to a dispersed state. The final concentration of MWNTs was 35 mg in 15 ml cyclohexane–Triton X-114 solutions. Next, 0.25 M $Zn(CH_3COO)_2$ or $Mg(CH_3COO)_2$ (Aldrich Chemicals, USA) solution was dropped into the above microemulsion system. The mixture was stirred at 40 °C for 2 hours. Finally, dilute NH_3H_2O solutions were added dropwise until the final pH reached 9. 50 ml ethanol was added into the reaction system and stirring was maintained for another 30 min. The precipitates were separated by three consecutive cycles of washing and centrifuging. The product was obtained after drying.



Scheme 1 Synthetic scheme for surface coverage of metal oxide nanoparticles onto MWNTs using water-in-oil microemulsions.

Previous studies[9] on the solubilization of SWNTs in water showed that the alkyl chain groups of NaDDBS adsorbed flat along the length of the tube. When the dispersed MWNTs were added into cyclohexane–Triton X-114, the hydrophilic head groups of NaDDBS and Triton X-114 would emerge due to their similar polarity, with the hydrophobic groups extended into the oil phase as shown in Scheme 1. Once metal acetate salt solutions were added into the microemulsions, they would reside in the water phase. Harimanow[10] reported that divalent metal cations such as Co(II), Mn(II), Cu(II) and Zn(II) could be extracted quantitatively by Triton X-114 in the absence of chelating ligands. According to their results, Triton X-114 extracts metal cations from the aqueous solution to the water/oil interface, and makes them accumulate at the interface gradually during the stirring process. With the addition of NH_3H_2O solutions, metal cations will precipitate from stable microemulsions.

Fig. 1 shows a typical TEM image depicting the attachment of hollow zinc hydroxide precursors to MWNTs. The particle size of the hollow particulates is about 10–20 nm. The precipitates appeared as hollow particles instead of the usual solid form. Because the precipitation reaction is very fast, metal cations that are rich at the interface will react with the precipitant (ammonia) as soon as possible and are solidified *in situ*. The TEM result correlated well with the proposed schematic process. Fig. 2 shows the EDS spectrum of the hollow particles. As well as the Zn and O peaks, a C peak also existed, suggesting the presence of an organic component originating from Triton X-114. After being calcined at

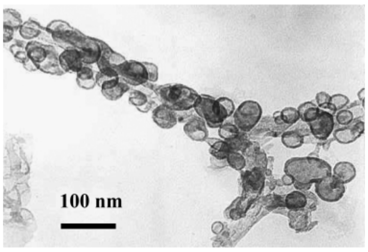


Fig. 1 Transmission electron micrograph of the as prepared zinc hydroxide precursors attached onto MWNTs.

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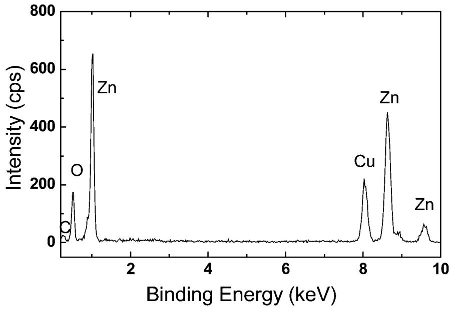

Fig. 2 EDS spectrum taken from the hollow particulates shown in Fig. 1. C, O and Zn were detected.

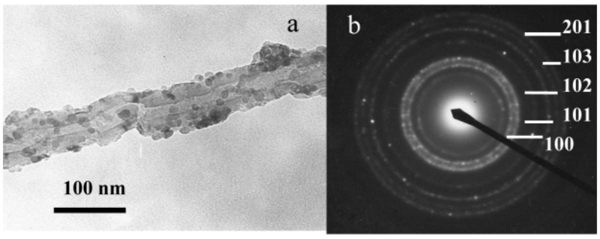

Fig. 3 Transmission electron micrographs of ZnO nanoparticles attached to MWNTs (a); SAED patterns of ZnO (b).

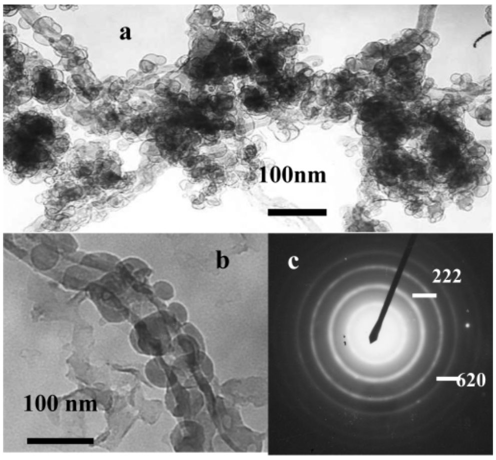

Fig. 4 Transmission electron micrographs of the as-prepared magnesium hydroxide precursors coating on MWNTs (a); MgO particles attached onto MWNTs (b); SAED patterns of MgO (c).

450 °C for 20 min, the hollow structure collapsed and transformed to well-crystallized ZnO nanoparticles as shown in Fig. 3. Particles with a mean size around 5 nm covered the surface of MWNTs homogeneously.

Very similar results have been obtained by using $Mg(CH_3COO)_2$ as coating source material. Magnesium hydroxide precursors formed hollow particles and attached onto MWNTs (Fig. 4(a)). After being calcined at 450 °C for 20 min, the hollow particulates transformed to crystallized MgO with particle sizes of 30–40 nm. These larger MgO nanoparticles are supposed to be agglomerates of smaller ones. Further studies involving the influence of the water-to-surfactant molar ratio and the composition of the aqueous component on the morphology of the coated particles are in progress. We expect the attachment of metal oxides to nanotube surfaces will promote better ceramic or other inorganic matrix-CNT adhesion and may lead to the development of homogeneous composites, thereafter improving mechanical and/or electrical properties.

In conclusion, we have demonstrated a strategy for functionalizing MWNTs noncovalently with inorganic nanoparticles, which is important for preserving the mechanical and electrical properties of carbon nanotubes. The water droplets act as a "binder" between MWNTs and nanoparticles, and their confinement in microemulsions produces nanoparticulates with less agglomeration and makes the coverage more homogeneous. In addition, the versatility of this method could be extended to other metal cations and it might be possible to cover CNTs with two or more components by choosing appropriate experimental conditions.

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